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Computer Simulation of Low Temperature Fuel Cells and their Components

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Modeling of Low Temperature Fuel Cells is a multi–disciplinary and multi–scale problem utilizing methods and techniques from mathematics, physics, chemistry and engineering. Some recent studies performed in our group at IWV-3 are summarized.

1 Introduction

Low temperature fuel cells such as the hydrogen-fed polymer electrolyte membrane fuel cell (PEFC) and the direct methanol fuel cell (DMFC) are regarded as promising technologies to replace combustion engines and batteries in mobile and stationary applications. Fuel cells convert chemical energy of combustion directly into electricity by spatial separation of anodic oxidation of fuel and cathodic reduction of oxygen. Protons generated at the anode migrate to the cathode, where they recombine with oxygen anions to form water. The reactions lead to the non-toxic products $\mathrm{H_2O}$ and $\mathrm{CO_2}$. The anodically generated electrons perform useful work on their external path to the cathode.

Forschungszentrum Jülich maintains a leading position in Europe in PEFC and DMFC research. As part of the Helmholtz community program on rational energy conversion our institute (IWV–3) performs a wide spectrum of research aimed at improving PEFC efficiency and at creating prototypes of commercial DMFC stacks in the 1 to 5 kW class. Modeling of components, single cells and stacks is an integral part of this effort. The technological goals are also supported by fundamental studies of the molecular mechanisms of species transport in polymer electrolyte membranes (PEMs) and of the kinetics of electrochemical reactions.

Prior to a broad introduction of fuel cell technology into the energy market substantial barriers still need to be overcome. These are, in the case of the PEFC

- low cell efficiency when using dry gases, which mandates elaborate humidification;
- cell flooding at high current densities due to a large amount of water produced at the cathode;
- the problem of catalyst poisoning by CO. This problem is critical for PEFCs with on–board reforming of liquid hydrocarbon fuels to hydrogen.

In the case of the liquid–fed DMFC the major problems are

- the slow kinetics of the methanol oxidation, leading to high voltage losses, high noble metal catalyst loadings and concomitant high costs;

- the high rate of methanol crossover through currently available membrane materials, which reduces cell power;
- flooding of the cathode catalyst layer due to the high electroosmotic flux of water through the membrane;
- large amount of gaseous CO_2 on the anode side, which reduces cell performance.

Last but not least, lowering the aging rate is crucial for commercialization of the cells of both types.

Fuel cell research and development thus has two aspects: The first one is the design of new components (catalyst layers, membranes and backing layers) with improved performance and lower cost. The second one is the proper assembly of these components into cells and stacks with high performance and low rate of aging.

Clarifying the transport mechanisms in the membrane and the mechanisms of the electrocatalysed chemical reactions in a fuel cell are subject of extensive experimental and theoretical work. Molecular dynamics simulations and quantum chemical calculations are indispensable tools in understanding these mechanisms. Transport parameters in the fuel cell components can be obtained by comparing the experimental data with the predictions of continuum models. This led us to studies of the following topics:

- Numerical modelling of DMFCs and PEFCs within the scope of continuum models.
- Classical molecular dynamics (MD) simulation of proton, water and methanol transport through polymer electrolyte membranes.
- *ab initio* MD simulation of methanol oxidation in the anodic catalyst layer.

In the first topic the fuel cell is considered as a whole, as a macroscopic "electrical machine". Here we aim at understanding the mechanisms of voltage loss in real cells and optimization of cell design. Modeling structure and dynamics on the atomic scale is performed in order to derive relationships between the macroscopic properties of materials, such as conductance, and the molecular motions.

2 Cell Simulations

A typical cross section of a polymer electrolyte fuel cell (PEFC) is sketched in the left part of Figure 1. The membrane electrode assembly (MEA) is clamped between two metal or graphite plates with the channels for feed gases supply, called the "flow field". The MEA usually consists of two gas–diffusion layers (GDLs) and two catalyst layers, separated by a proton conducting membrane.

Current production in a cell induces fluxes of gases, liquid water, heat and charged particles. The distribution of the respective parameters (concentrations, fields etc.) is usually very non–uniform. Furthermore, the characteristic scale of the parameter variation ranges from several micrometers (the thickness of the catalyst layer) to several meters (the length of the channel). In general, the problem of fuel cell modeling is multi–scale and multi–dimensional.

Several approaches to model such a system exist. The number and complexity of the processes in the MEA together with sophisticated geometries of the flow fields almost inevitably lead to 3D CFD models. Differently, our quasi–3D (Q3D) model of a PEFC[1] is based on the following idea. In many cases one may neglect the in–plane fluxes in the MEA. The full 3D problem (Figure 1) can then be split into a problem of flow in the channel and a 2D problem in the MEA cross–section, as shown in Figure 1. The channel problem provides concentrations of reactants for the problem in the MEA. The latter returns local current density required to calculate the profiles of reactants concentration along the channels. Both problems are, therefore, coupled and the solution has to be determined iteratively[1].

Furthermore, the cell cross-section consists of a number of geometrically identical elements (Figure 1). This allows an efficient code parallelization. The physical model is formulated for a single element (2D element in Figure 1). The code is then replicated, so that each element "is solved" on a separate processor. Upon completion of an iteration step the elements exchange with the "boundary conditions", as shown on the right side of Figure 1. The cross-section of a typical cell contains several tens of such elements; the time of simulation of such a system is only 2–3 times larger than the time of simulation of a single element. This algorithm efficiently exploits the capability of a massively parallel computer system.

The typical solution is shown in Figure 2. Note that to represent the details the scale of this figure is strongly distorted: the size of the computational domain along x–axis is about 1 mm, whereas along y–axis its size is about 21 cm (Figure 2). The two elements at the inlet are "zoomed" in Figure 3.

Figures 2 and 3 show that there are three types of non–uniformities in a cell. The first is a small–scale non–uniformity (maps of Q_c and σ_m) in the through–plane direction. Proton conductivity of the catalyst layers is rather poor and the electrochemical reaction is largely confined to the region close to the membrane interface, where protons are "cheaper" (i. e., found with higher probability). Analysis of the governing equations shows, that this regime of the catalyst layer operation leads to high polarization losses[2].

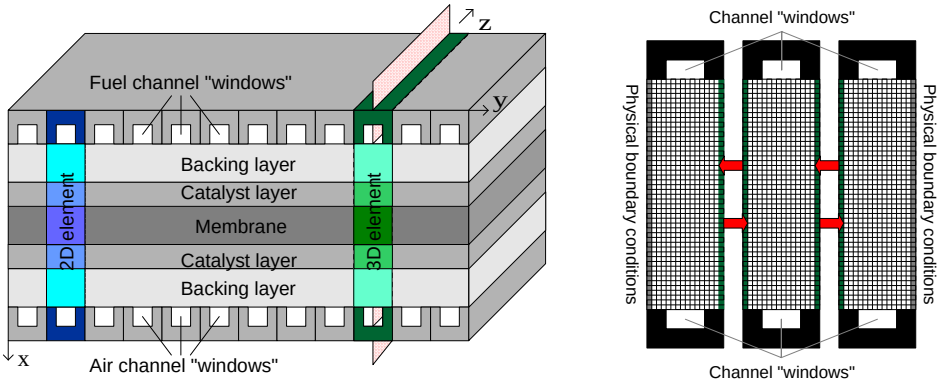

Figure 1. Left: Sketch of the fuel cell. Right: The idea of parallelization. Adjacent cell elements exchange with the "boundary conditions" upon completion of an iteration step.

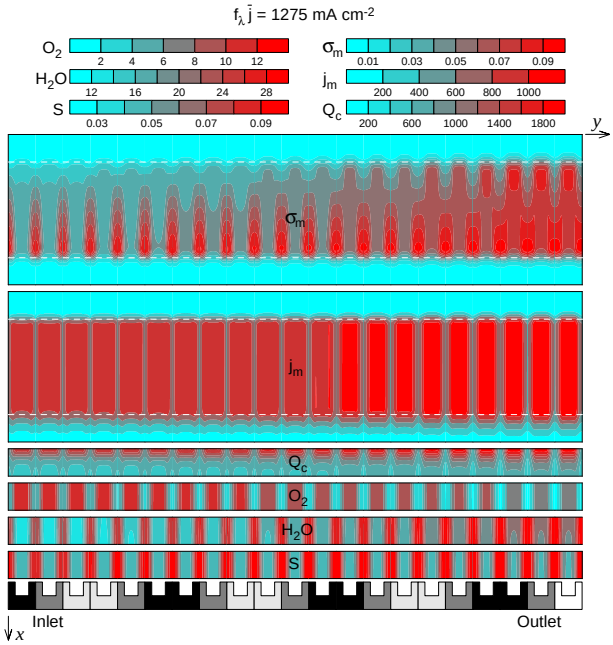

Figure 2. 3D maps of the PEM fuel cell[1]. Shown are (top to bottom): proton conductivity σ_m (Ω^{-1} cm^{-1}) and proton current density j_m (mA cm^{-2}) in membrane and catalyst layers, the rate of the electrochemical reaction Q_c (A cm^{-3}), oxygen and water molar concentrations (10^{-6} mole cm^{-3}) and liquid saturation in the cathode catalyst layer. White dashed lines indicate the membrane/catalyst layers interfaces.

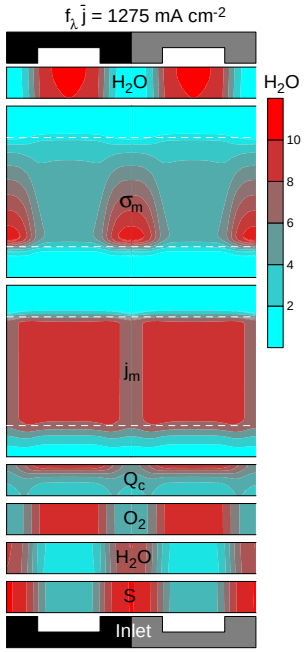

Figure 3. The same as in Figure 2 plus liquid saturation in the anode catalyst layer (on top) in two elements at the inlet. For the notations and scales please see Figure 2.

Proton conductivity of the bulk membrane is higher at the cathode side and lower at the anode side (Figures 2,3) due to proton–driven electroosmotic flux of water (from the anode to the cathode side). Back diffusion of water does not fully compensate the electroosmotic flux and the anode side of the membrane is dried. In this particular regime of cell operation the membrane drying limits the current, due to the poorer membrane conductivity at low water content (see below).

The second is a medium–scale non–uniformity due to the alternation of channel "windows" and current collector ribs along the y–axis (Figures 2,3). Oxygen transport to and water transport from the regions above the ribs is poor; thus water tends to accumulate there and lack of oxygen reduces the rate of the reaction in these domains (Figures 2,3).

The third is a large–scale non–uniformity due to oxygen exhaustion and accumulation of water along the channel. Close to the outlet the membrane is well humidified, though the last elements experience "oxygen starvation" (Figure 2).

The problem of this particular cell design is to mitigate the negative effect of non–uniformities of all three types. The non–uniformity of the reaction rate across the catalyst layer can be diminished by increasing the proton conductivity of the layer. Medium–scale non–uniformity (channel / rib) can be reduced by increasing oxygen and water diffusivity in the backing layer, i.e., by enlarging its porosity. Large–scale non–uniformity can be diminished by increasing the oxygen stoichiometry of the cathode flow.

The results thus give hints how to improve cell design and help to optimize operating conditions. Besides, Q3D simulations provide invaluable information for construction of simplified analytical and semi–analytical models of a cell[3]. These *fast* models can be used for rough characterization of cells. Comparison of analytical, numerical and experimental data gives a much more reliable information, than any single model. We believe that in the near future the approach based on such a hierarchy of models will play a substantial role in fuel cell studies.

3 Proton Transport in Membranes

PEMs like Nafion are phase-separated on the nanometer scale into a polymer phase consisting of a polytetrafluoroethylene backbone with pendant end-group sulfonated side chains and an aqeuous phase. The (continuous) polymer phase provides the structural stability for separating anodic and cathodic compartments. It is experimentally well established that above a percolation threshold, when the aqueous phase is thought to become continuous, proton conductance in Nafion or related materials increases significantly with water content λ (λ is the ratio of water molecules to sulfonate groups). The sulfonic acid groups are strongly acidic so that protons become solvated and conducting in the aqueous phase. From the magnitude and the temperature dependence of the experimental proton conductance in fully humidified Nafion membranes (where $\lambda \approx 14$) it has been concluded that the proton transport mechanism follows the well-established proton-hopping or structural diffusion mechanism characteristic for the high proton mobility in bulk acids. At low water content ($\lambda \approx 3 - 5$) the proton transport mechanism is best described by an interplay between a surface mechanism (transfer along the sulfonate groups) and the bulk mechanism[4].

Describing (i) the structural complexity of the biphasic polymer / water material and (ii) the bond-forming and -breaking nature of the elementary act of proton transfer can best be reconciled by modeling the materials using so-called empirical valence bond (EVB)

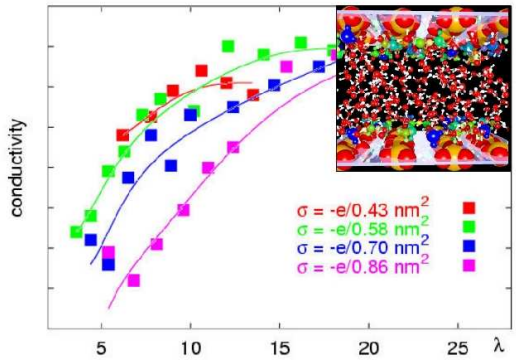

Figure 4. Dependence of proton conductivity (scaled units) on water content λ for several slab pores with different surface charge densities (spacings) of sulfonate groups. Note that the variance of instantaneous proton states (blue: H_3O^+-like, yellow-green: $H_5O_2^+$-like) in the snapshot is characteristic for the aqueous pores, and their easy interconversion is essential for proton mobility, thus warranting the use of complex molecular models.

interaction potentials. In such a model, the proton can be regarded as being in a superposition state between different valence bond states, in which an excess proton belongs to one of a subset of water molecules. In the most simple form, only two resonance states $\phi_1 : H_3O^+ \cdots H_2O$ and $\phi_2 : H_2O \cdots H_3O^+$ are considered. In one state the proton is localized on the first oxygen, in the other one on the second hydrogen. Using a configuration-dependent coupling between these two states, one can describe proton transfer as a continuous sequence of $H_5O_2^+ \rightarrow H_3O^+ \rightarrow H_5O_2^+ \rightarrow H_3O^+$transitions. Besides being conceptually simple, such an empirical valence bond force field allows the simultaneous simulation of many protons over time periods of nanoseconds, i.e., the minimum requirements for studying a concentrated proton solution in a disordered polymer framework[5].

Taking the most extreme viewpoint, one can treat the polymer as an immobile framework with simple pores of slab or cylinder shape, in which proton transport can be studied as function of a variety of *generic* structural and dynamical features of the polymer (such as acid strength, head group and side chain mobility, equivalent weight) and *operational* parameters of the working fuel cell (such as temperature and water content). Here, the power of a massively parallel computer can be harnessed for parallelization on the level of the single simulation, each one of which typical lasts 2-3$\cdot 10^7$ relatively short time steps (Per step parallelization based on domain decomposition or interaction decomposition is not very effective due to communication overheads.) Figure 4 shows, as an example, the calculated dependence of proton conductance on water content for different equivalent weights of the polymer (which is modeled by the spacing of sulfonate groups on the slab wall)[5]. It demonstrates how the single pore mobility leads to the water-content dependent proton conductance in PEMs that was mentioned above.

On the basis of the temperature dependence of proton mobility in single pores it was concluded that the experimentally observed behavior is most likely associated with the dynamics of the polymer at low water content. In a next generation of models, local pore structure and dynamics was investigated using a fully atomistic model of the Nafion polymer, employing for the aqueous phase a simple classical force field which treats hydronium and water like rigid molecular ions or molecules interacting through standard force fields[6]. Such simulations can be conveniently parallelized by decomposing the system into several equivalent interacting subsystems of identical composition. Since meaningful results can be collected only from a series of runs at different temperatures and for different water

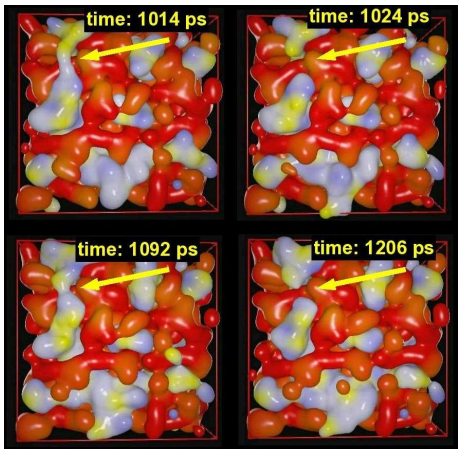

Figure 5. Snapshots at different times of a jelly-bean representation of a simulated mixture of water and Nafion in protonated form (at water content $\lambda = 5$). Red regions denote polymer, grey, blue and yellow regions denote water, hydronium and sulfonate groups, respectively, in the aqueous phase. The indicated box corresponds to a length of 4.5 nm. Note that the jelly-bean surfaces hide a large number of molecules [E. Spohr, work in progress].

contents, distribution of the jobs over 2–4 processors made optimal use of the allocated resources at NIC. As a representative result of these studies, Fig. 5 shows time dependent snapshots of aqueous domains at $\lambda = 5$, which are consistent with the view of activated fluctuative bridging of the aqeous pores, reducing the overall proton conductance as well as increasing the activation energy. With atomistic simulations on the united-atom level, where only the essential topological features of the Nafion base unit are retained, morphological transitions between inverse micellar aqueous pores at low water content to channel like structures at high water content are currently studied.

4 Methanol Oxidation on Noble Metal Catalysts

The protons in the membrane originate from electrocatalytic processes in the anodic catalyst layer. In the DMFC these processes are, to some extent, performance limiting. At least, they mandate high noble metal catalyst loadings and concomitant high device costs. We have thus investigated the catalytic oxidation of methanol in realistic, i.e. fuel cell-relevant environments, using quantum mechanical density functional theory to describe

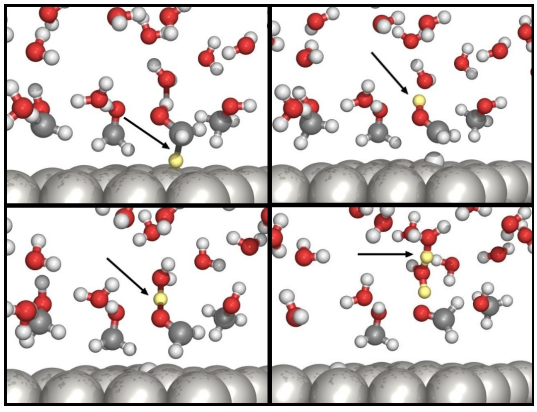

Figure 6. Chemical reaction dynamics of methanol oxidation to formaldehyde: One of the C–H bonds of the methyl group becomes elongated (top left) and eventually breaks (top right). The adsorbed hydrox-methyl group stabilized by forming a hydrogen bonded complex to a water molecule (bottom left) and dissociates rapidly into adsorbed formaldehyde and a hydronium ion (bottom right) which further stabilized by undergoing structural diffusion steps to form Zundel ions $H_5O_2^+$.

the coupling between electronic structure and nuclear dynamics. As a starting point, we considered the oxidation of adsorbed methanol at a water / platinum interface. For our calculations we have employed the VASP package[7] which showed for our purposes good scaling characteristics up to 8 processors per job, and allowed us to perform *ab initio* molecular dynamics calculations of uncharged and charged interfaces. Water did not only influence the reaction pathway as compared to the corresponding gas phase reaction, it actively changed the sequence of reactive events by directly, i. e., without intermediate adsorption, incorporating hydrogen ions into its hydrogen bond network, as illustrated in Fig. 6 (see Ref.[8]). These calculations are currently extended to investigate the influence of fuel cell environment on the later oxidation steps.

5 Concluding Remarks and Outlook

Modeling of transport processes in low temperature fuel cells is a true multidisciplinary and multi–scale effort, which requires joint efforts by physicists, chemists, applied mathematicians and engineers. In our group at IWV-3 we tightly integrate analytical theory[3] together with our computational studies into FZJ's research and development of viable fuel cell technology. In spite of dramatic progress in computer technology some key problems in PEFC and DMFC fuel cell technology remain unsolved, largely due to the extremely complicated media and materials used in fuel cells, in which the physics of species transport is still not completely understood. Bringing these "electrical machines" to market is a challenge not only for experimental research but also for "silicon machines" such as NIC's Regatta system.

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